# CHEMICAL SENSOR USING CHEMICALLY INDUCED ELECTRON-HOLE PRODUCTION AT A SCHOTTKY BARRIER

## BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

[0002] The field endeavor of the invention relates to sensors for detecting chemicals and in particular to a sensor for detecting and distinguishing atomic hydrogen or atomic deuterium oxygen, carbon monoxide, and nitric oxide.

[0003] 2. Description of the Prior Art

[0004] Electron transport through a metal-semiconductor interface is determined largely by the Schottky barrier between them.

[0005] The detailed pathways of energy transfer in exothermic and endothermic reactions at metal surface is incompletely understood and of fundamental interest. Bond formation energy of up to several electron volts is transferred into the substrate during such exothermic reactions. Since bulk phonon energies are typically two orders of magnitude smaller, it has been appreciated by the prior art that non-adiabatic excitations of electron-hole pairs may be an alternative to the creation of multiple phonons as a mechanism for sensor detectors. With surface reactions at thermal collision energies, there are few examples of energy transferring to the electronic system accompanied by light emission or chemiluminescence and exoelectron ejection. Chemiluminescence and exoelectron injection are observed only with exothermic adsorption of electronegative molecules on reactive metal surfaces. In addition, exoelectron emission requires that the metal have a low work function. Heretofore, there has been no direct experimental evidence for adsorption induced electron-hole pair excitations at transition metal surfaces.

[0006] Therefore, what is needed is some type of sensor design or principal in which adsorption induced electron hole pair excitations at a transition metal surface can be exploited to provide a chemical sensor.

## BRIEF SUMMARY OF THE INVENTION

[0007] The invention is a silicon device structure, or more specifically a metal-semiconductor Schottky diode, which exploits the current-voltage characteristics of the diode for separation of charge and the interaction of the surface adsorbates on the metal to produce electrons or holes of sufficient energy to transverse the ultrathin metal film and cross the Schottky barrier. The structure allows reliable, zero force electrical contacts to be made to metal films less than 100 Angstroms thick. In one embodiment two metalized contacts are deposited using photolithographic techniques on a 4000 Angstrom oxide layer prepared on Si (**111**). The oxide is etched from between the contacts and the exposed 6 mm×6 mm Si (**111**) surface is wet chemically treated. Under vacuum conditions ultrathin metal is deposited onto the device to form a diode under well defined conditions.

[0008] The sensor device may be microfabricated on n- or p-doped semiconductor wafers. In the illustrated embodiment $\rho_n$=5-10 Ω cm, $\rho_p$=1-20 Ω cm), in an ohmic contact is provided on the back of wafer by means of by $As^+$ and $B^+$ ion implantation, respectively. Isolated from the silicon, the thick gold contact pads are evaporated on a 4000 angstrom thermal oxide layer on the opposing or front side of the device. A 0.3 $cm^2$ window is chemically wet etched through the oxide layer between isolated the gold pads through the use of buffered hydrofluoric acid leaving a clean, passivated silicon surface. The device is then transferred into an ultra-high vacuum chamber ($p \approx 10^{-8}$ Pa) for metal deposition and measurement.

[0009] Copper and silver films, for example, are deposited by e-beam evaporation at substrate temperatures of 135° K. The nominal thickness is measured by a quartz microbalance. The etching of the oxide produces an angle of inclination between the oxide and the top surface of the silicon substrate with typically 25°. The evaporated thin metal films are connected to the thick gold pads across the small inclination angle to provide a zero force front contact to the device. This contact design allows electrical contact for the current/voltage measurements between the front contacts and back contact even with film thicknesses below 80 angstroms.

[0010] In preliminary experiments investigating the energy transfer during chemisorption, a new process has been discovered associated with chemisorption of atomic hydrogen or atomic deuterium on Ag and Cu ultrathin films. When these metals are deposited (30 Angstroms −150 Angstroms) onto Si(**111**) in a Schottky diode detector structure, a current is generated associated with an incident atomic H or D beam on the film. It is hypothesized that this "chemicurrent" is a result of chemisorption induced excited charge carriers which traverse the Schottky barrier. That energy transfer from chemisorption can proceed by direct electronic excitation is a significant departure from the conventional dogma which holds that multiple phonon excitation is the means through which the heat of adsorption is dissipated.

[0011] The implications of this observation for the study of surface catalyzed reactions are many. In addition, this process serves as a basic link between chemical processes and electronics and offers the potential for the generation of unique electronic signatures for chemical reactions and the creation of a new class of solid-state chemical sensor. The first direct means of measuring atomic H or atomic D separate from the diatomic molecule is demonstrated below. More importantly, it may also be possible to differentiate H from D on the basis of the signal. It is expected that there are unique chemicurrent signals associated with many types of surface reactions.

[0012] Hot electrons and holes created at a transition metal surface, such as a silver or copper surface by adsorption of thermal hydrogen and deuterium atoms can be measured directly with ultrathin-metal film Schottky diode detectors on silicon (**111**) according to the invention. When the metal surface is exposed to these atoms, charge carriers at the surface and travel ballistically toward the interface. The charge carriers are detected as a chemicurrent in the diode. The current decreases with increasing exposure and eventually reaches a constant value at a steady state response. The invention uses the first discovery of a non-adiabatic energy dissipation during adsorption at a transition metal surface as a means of providing a chemical sensor or thin film "nose" able to sniff out the presence of chemicals.

[0013] The mechanism of the invention is based on the speculation that although the maximum energy of any hot